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Improvement in tribological properties of chromium oxide coating at high temperature by solid lubricants

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Abstract

The aim of the investigations was to improve the tribological properties of chromium oxide (Cr₂O₃) coating for applications in heat engines at high temperatures. The experimental results show that the solid lubricants CaF₂ and BaF₂ in composite coatings can reduce and stabilize the friction coefficient, decrease the wear rate, prevent surface damage and improve the load capacity of Cr₂O₃ coating at 425 °C in air. In tribotests at 0.2–1.0 MPa it appears that the optimal solid lubricant content is around 14%–21% for Cr₂O₃–CaF₂ coatings and 20%–31% for Cr₂O₃–BaF₂ coatings. Auger electron spectroscopy and energy-dispersive spectroscopy analyses show that the friction coefficient is correlated with the amount of solid lubricant in contact areas: the friction coefficient decreases with solid lubricant content if it is less than 2%–4%, then stabilizes at about 0.20–0.25.

1. Introduction

Plasma-sprayed ceramic coatings such as zirconia and alumina have been applied to the combustion zone surfaces of different engines. They can ensure good thermal protection for components such as pistons, valves, upper liners, etc. The resulting improvements in engine durability and performance that have been experienced are significant and have led to increasing interest in the subject [1, 2]. However, the reduction in heat transfer resulting from the use of ceramic parts leads to a greater temperature rise in the cylinder walls of engines. These high temperatures, exceeding the cracking point of organic lubricants, generate dry sliding conditions between the liner and the piston ring [3]. In such cases the metallic parts cannot work because of their poor tribological properties under non-lubricated conditions at high temperatures. Consequently, an important task is to improve the tribological performance at high temperatures.

Ceramics, because of their good refractory properties, high hardness and good corrosion resistance, were considered as prospective candidate materials. Over a period of several years a large number of investigations have been carried out using different kinds of ceramics [4-8]. In comparison with metallic materials, ceramics have certainly improved the tribological performance, but the friction coefficient and wear rate of these materials are still too high for successful applications.

In order to improve the tribological properties of ceramics under severe sliding conditions, we have incorporated solid lubricants in the form of plasmasprayed composite coatings [9]. The philosophy of these investigations is to exploit the high hardness of the ceramic matrix and the good properties of the solid lubricant.

The ceramic used in these studies is chromium oxide (Cr₂O₃). It was selected according to the results of our experimental investigations [10, 11]. The solid lubricants used are calcium difluoride (CaF₂) and barium difluoride (BaF₂). They are considered as having good thermal and chemical stabilization and a strong lubrication effect [12].

2. Experimental details

2.1. Materials

The commercial Cr₂O₃ powder used in these investigations has been produced by melting and crushing techniques. The experimental CaF₂ and BaF₂ powders have been developed by Rhône Poulenc; scanning electron microscopy (SEM) shows that both powders consist of angular and spongy particles. Table 1 presents some of their technical characteristics.

The composite coatings have been obtained by the atmospheric plasma spraying of powder mixtures on a mild carbon steel (35CD4) substrate that had been sand blasted with corundum. In order to improve the

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Powder	Chemical composition (wt.%)	Powder description	Particle size (µm)
Cr ₂ O ₃	94.97 Cr ₂ O ₃ , 3 Fe, 1 Cr, 0.55 S. 0.45 Ca, 0.03 Mo	·	3070
CaF ₂	94 CaF ₂ , 1.65 Si, 0.5 Mg, 0.09 Al, 0.03 Fe, 0.01 Mn, 0.01 Cu	Angular, spongy	70
BaF ₂	96.91 BaF ₂ , 0.33 Si, 0.01 Mg, 0.05 AI, 0.05 Fe, 0.93 Sr, 0.09 Ca, 0.335 O, 0.055 C	Angular, spongy	10

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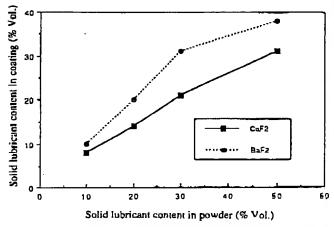
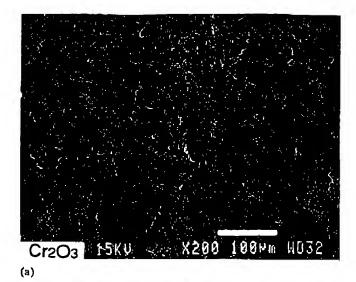


Fig. 1. Correlation between solid lubricant contents in powder mixtures and composite coatings.

adherence of the coatings to the substrate, a bond coating of 80 μ m depth of pure Cr_2O_3 was sprayed before deposition of the composite coating.

Chemical analysis shows that the solid lubricants are partially lost during spraying, especially for the Cr_2O_3 — CaF_2 coatings, mainly because of the difference in their fusion points, which results in different evaporation rates. Figure 1 shows the correlation between the solid lubricant content of the powder mixture and that of the composite coating. Generally, this loss will increase with increasing solid lubricant percentage: the solid lubricant content in the coatings varies from 8% to 34% CaF_2 for the Cr_2O_3 — CaF_2 coatings and from 10% to 38% BaF_2 for the Cr_2O_3 — BaF_2 coatings when the solid lubricant content in the powder mixture varies from 10% to 50%.

The coated surfaces have been observed by SEM. Some typical images are shown in Fig. 2. The composite coatings consist of a ceramic matrix (Cr_2O_3) and solid lubricant particles dispersed in the matrix. The particle size is generally about 10 μ m, but some of them can be more than 100 μ m. Their shape is spheroidal. On the surface of the coatings we have observed some open pores. Statistical analysis of the Cr_2O_3 — CaF_2 coatings shows that the porosity increases with increasing



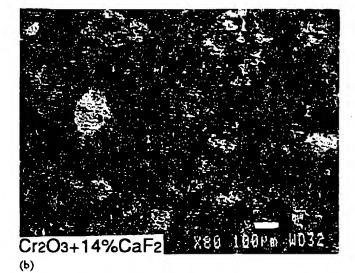




Fig. 2. Initial microstructures of coatings: (a) Cr_2O_3 , (b) $Cr_2O_3-14\%CaF_2$, (c) $Cr_2O_3-20\%BaF_2$.

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solid lubricant content. Consequently, the coating density decreases and the roughness of the ground surface

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lubricant content.

Before sliding, we measured the Vickers hardness of the polished cross-section and of sliding surfaces with different roughnesses; i.e. ground and polished sliding surfaces. Figure 3 presents the hardness results. Although there is some scatter among these measurements due to differences in the roughness and structure as well as in the nature of the solid lubricants, we have found that the hardness decreases with increasing solid lubricant content and that the hardness of the Cr₂O₃-BaF₂ coatings is slightly lower than that of the Cr₂O₃-CaF₂ coatings.

of the composite coating increases with increasing solid

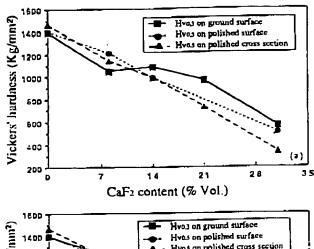
In order to minimize the influence of the surface roughness on the friction and wear of the coatings, the sliding surface was lightly polished with abrasive paper of mesh 1000# to obtain samples with the same R_a (0.4 μ m for the Cr₂O₃ coating and 0.6 μ m for the Cr₂O₃-CaF₂ and Cr₂O₃-BaF₂ coatings). Before each test the samples were rinsed with denatured ethyl alcohol.

2.2. Apparatus and experimental conditions

All experiments were carried out using a tribometer specially designed for investigations of friction and wear in air at high temperatures [13, 14]. Its schematic description is given in Fig. 4. Rotation is provided by a spindle linked to an electric motor. Sliding occurs between two plasma-coated cylindrical ring surfaces of area 286 mm2 which are mounted on a stationary and a rotary spindle respectively. Normal load is applied through the stationary spindle by dead-weights hung on the loading arm when the normal load required is small (less than 0.55 kN) and by a pneumatic system when the normal load is larger (0.55-6.5 kN). The samples are heated to the required temperature, as measured by the thermocouples, using an electric furnace. The stationary spindle is restricted by a torquesensing system which measures the friction coefficient at high temperatures (20-1100 °C). The friction force is recorded continuously.

All tests were carried out under the following conditions: environment, atmospheric air; temperature, 425 °C; sliding velocity, 0.1 m s⁻¹; contact pressure, 0.1-22.1 MPa, corresponding to a normal load of 28.6 N-6.32 kN.

The total sliding time for most experiments was 6 h. Damage processes were followed by optical microscopy and SEM, interrupting the motion after 0.5, 2 and 4 h of sliding. Wear was characterized from the mass loss of both discs after taking into consideration the oxidation weight gain of the metallic substrate (see Appendix).



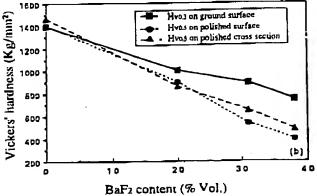


Fig. 3. Evolution of Vickers bardness of (a) Cr₂O₃-CaF₂ and (b) Cr,O3-BaF2 with solid lubricant content.

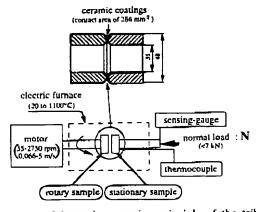


Fig. 4. Schematic operating principle of the tribometer.

3. Experimental results

Five friction couples - Cr₂O₃/Cr₂O₃, Cr₂O₃/Cr₂O₃- $CaF_{z}, Cr_{z}O_{3}-CaF_{z}/Cr_{z}O_{3}-CaF_{z}, Cr_{z}O_{3}/Cr_{z}O_{3}-BaF_{z}$ and Cr2O3-BaF2/Cr2O3-BaF2 - have been tested. The results will be presented in terms of the following three

- (1) improvement in tribological properties of Cr2O3 coating by solid lubricant addition;
- (2) influence of solid lubricant content, nature and distribution on friction coefficient and wear rate;

(3) tribological properties of the coatings under high pressure.

3.1. Improvement in tribological properties of Cr2O3 coating

Comparing the friction and wear of Cr₂O₃/Cr₂O₃ with those of the other couples, we find that the solid lubricants improve the tribological properties of the Cr₂O₃ coating. Figure 5 shows typical friction curves of tribotests carried out under the same conditions. Two observations can be derived from them. Firstly, for the friction of pure Cr2O3 the stick-slip phenomenon occurs and a considerable variation in the friction coefficient is observed. When a solid lubricant is introduced in one or both coatings, the variation in the friction coefficient becomes much smaller and the stick-slip phenomenon disappears. Secondly, the mean friction coefficient without solid lubricant is about 0.4, but it is much smaller and varies between 0.2 and 0.25 if there is a solid lubricant in the coating(s).

Figure 6 presents the evolution of mass loss vs. sliding distance under a pressure of 0.2 MPa. It shows that this evolution can be distinguished by two different

- (1) At the beginning of a test the mass loss is significant. Microscopic observations show that this results from surface polishing, which produces considerable wear because of the removal of some sharp asperities. For the test under pressures between 0.2 and 1.0 MPa this stage is shorter than 30 min.
- (2) After the running-in stage the wear of the coating becomes more stable and regular and the mass loss increases linearly. To evaluate the wear resistance of different coatings, we have used the "wear rate K_v " term, which is defined by the formula

$$K_{r} = \frac{\Delta m}{\rho PSVt}$$

where Am is the mass loss of the two samples of one couple, ρ is the mean density of the coatings, P is the apparent pressure, S is the nominal contact area, V is the sliding velocity and t is the sliding time.

Table 2 presents wear rates and mean friction coefficients of different couples under pressures of 0.2, 0.5 and 1.0 MPa. It is seen that the solid lubricants can reduce the wear rate considerably.

Figure 7 presents photographs of the surfaces of Cr_2O_3 , $Cr_2O_3-14\%CaF_2$ and $Cr_2O_3-20\%BaF_2$ after 6 h of sliding under a pressure of 0.2 MPa against Cr₂O₃. They show that the Cr2O3 surface after sliding against Cr.O. has been damaged and is characterized by the removal of material in some contact areas with strong adhesion. However, when a solid lubricant is introduced in the coating(s), the surfaces of the samples made of Cr2O3 and Cr2O3-solid lubricant become macroscopi-

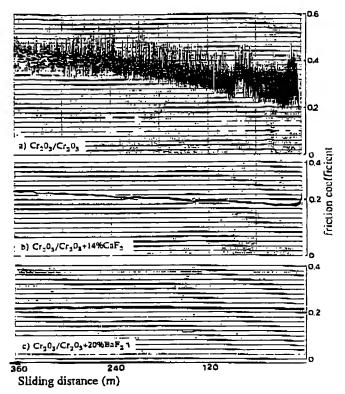


Fig. 5. Friction curves under 0.2 MPa.

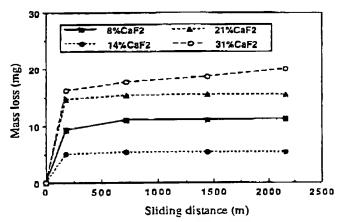


Fig. 6. Variation in mass loss with sliding distance for Cr2O3-Cr2O3-CaF2 under 0.2 MPa.

cally very smooth, while microscopically they are characteristic of the formation of contact plateaux via plastic deformation; we have not observed any extensive surface damage.

3.2. Influence of solid lubricant content, nature and distribution

3.2.1. Influence of solid lubricant content

The solid lubricant content exerts an important influence on the tribological properties. Figure 8 presents the variations in friction coefficient and wear rate

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TABLE 2. Mean friction coefficient f, friction coefficient dispersion amplitude Δf and wear rate K, under 0.2, 0.5 and 1.0 MPa

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Friction materials*	Contact pressure (MPa)									
	0.2			0.5			1.0			
	f	Δf	K. (10 ⁻⁶ mm ³ N ⁻¹ m ⁻¹)	f	Δf	K. (10 ⁻⁶ mm ³ N ⁻¹ m ⁻¹)	f	Δf	K. (10 ⁻⁶ mm ³ N ⁻¹ m ⁻¹)	
Cr_2O_3/Cr_2O_3	0.42	0.1	6,5	0.35	0.04	6.1	0.32	0.02	5.0	
Cr ₂ O ₃ /Cr ₂ O ₃ -x%SI	•									
SL: CaF ₂ x = 8 14	0.25 0.25	0.00 <i>5</i> 0.003	0,23 0,16	0.30	0.006	0.66	0.58	0.008	4.1	
21	0.26	0.003		0.26	0.003	0.13	0.27	0.003	0.06	
34	0.26	0.004	0.05 4.7	0.23 0.26	0.003 0.004	0.25	0.26	0.003	0.12	
						3.0	0.26	0.005	1.9	
SL: $BaF_2 = 10$	0.29	0.004	0.51	0.25	0.004	0.12	0.27	0.005	0.06	
20	0.24	0.003	0.88	0.24	0.003	0.13	0.25	0.003	0.02	
31	0.25	0.003	0.09	0.22	0.003	0.06	0.23	0.003	0.12	
Cr2O3-4%SL/Cr2O3	-x%SL				•					
SL: CaF, x=14	0.27	0.004	0.08	0.27	0.004	0.07	0.28	0.004	0.3	
21	0.27	0.004	0.13			****	-12-5	2.207	0.5	
34	0.27	0.004	5.6	0.26	0.004	1.7	0.25	0.004	2.7	
SL: $BaF_2 x = 20$	0.27	0.003	0.09	0.27	0,003	0,09	0,27	0.003	0.03	
31	0.26	0.003	0.08	0.25	0.003	0.07	0.27	0.003	0.06	
38	0.26	0.003	0.85	0.24	0,003	0.12	0.23	0.003	0.62	

^{&#}x27;SL, solid lubricant.

vs. CaF₂ content for friction of the Cr₂O₃/Cr₂O₃-CaF₂ couple, while Fig. 9 presents those for the Cr₂O₃-BaF₂/ Cr₂O₃-BaF₂ test. They show that a low solid lubricant content generally produces a high friction coefficient and a substantial wear rate. On increasing the solid lubricant content, the friction coefficient first decreases and then stabilizes at about 0.2-0.25. However, we have observed optimal content ranges for the wear rate: 14%-21% CaF₂ for Cr₂O₃/Cr₂O₃-CaF₂ sliding and 20%-31% BaF₂ for Cr₂O₃-BaF₂/Cr₂O₃-BaF₂ sliding. These phenomena can be explained by the different influences of the solid lubricant on the tribological and mechanical properties of the coatings; an increase in the solid lubricant percentage can certainly improve the tribological properties, but it also produces a degradation in the mechanical properties. This is the reason why coatings with a medium content of solid lubricant show the best performance.

3.2.2. Influence of solid lubricant nature

Figure 10 compares the friction coefficients and wear rates of $Cr_2O_3/Cr_2O_3-x\%CaF_2$ sliding with those of $Cr_2O_3/Cr_2O_3-x\%BaF_2$ (x is the solid lubricant content by volume in the powder mixtures). It shows that the sliding friction coefficient of $Cr_2O_3/Cr_2O_3-x\%BaF_2$ is slightly lower than that of $Cr_2O_3/Cr_2O_3-x\%CaF_2$, while their wear rates show the same trend. This small difference between the two kinds of solid lubricant may

result from their different hardnesses, i.e. the hardness ratios of Cr₂O₃ and the solid lubricants will be different, which will result in a slightly different friction coefficient [15].

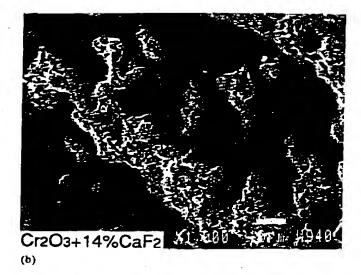
3.2.3. Influence of solid lubricant distribution

Figure 11 compares the friction coefficients and wear rates of $Cr_2O_3/Cr_2O_3-x\%CaF_2$ sliding with those of $Cr_2O_3-x\%CaF_2/Cr_2O_3-x\%CaF_2$ (x is the solid lubricant content by volume in the coatings). Generally, $Cr_2O_3/Cr_2O_3-x\%CaF_2$ has a lower sliding friction coefficient than $Cr_2O_3-x\%CaF_2/Cr_2O_3-x\%CaF_2$, while their wear rates are of the same magnitude. Similar phenomena have been observed in sliding with $Cr_2O_3-x\%BaF_2$ coatings. Figure 12 compares the friction coefficients and wear rates of $Cr_2O_3/Cr_2O_3-x\%BaF_2$ sliding with those of $Cr_2O_3-x\%BaF_2/Cr_2O_3-x\%BaF_2$ (x is the solid lubricant content by volume in the coatings).

3.3. Tribological properties of the coatings under high pressure

It is very important to determine the maximal pressure of the coatings for applications. For this purpose we have measured the friction coefficients and wear rates of Cr₂O₃/Cr₂O₃ and Cr₂O₃/Cr₂O₃-14%CaF₂ sliding under high pressures up to 22.1 MPa and generally confirmed the reduction in friction coefficient and wear rate by solid lubricant addition even under high pressure.

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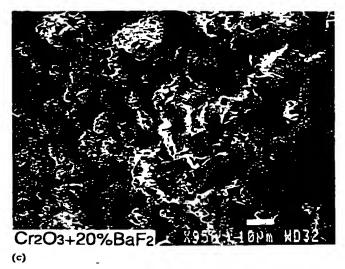


Fig. 7. Surface damage of (a) Cr_2O_3 , (b) $Cr_2O_3-14\%CaF_2$ and (c) $Cr_2O_3-20\%BaF_2$ after 6 h of sliding against Cr_2O_3 under 0.2 MPa.

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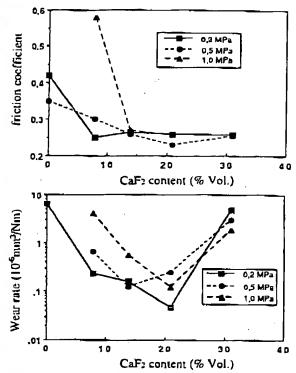


Fig. 8. Evolution of friction coefficient and wear rate of Cr_2O_3/Cr_2O_3 -CaF2 with CaF2 percentage.

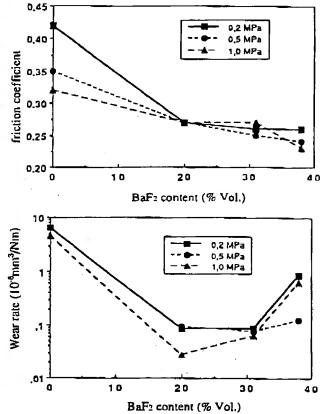
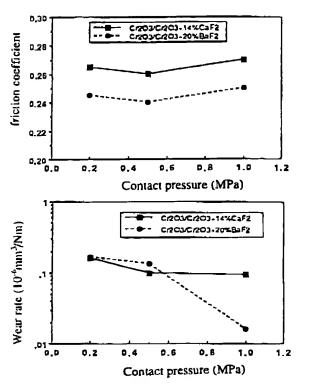


Fig. 9. Evolution of friction coefficient and wear rate of Cr₂O₃-BaF₂/Cr₂O₃-BaF₂ with BaF₂ percentage.

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Fig. 10. Comparison of friction coefficient and wear rate of Cr₂O₃/ Cr₂O₃-14%CaF₂ and Cr₂O₃/Cr₂O₃-20%BaF₂ under 0.2 MPa.

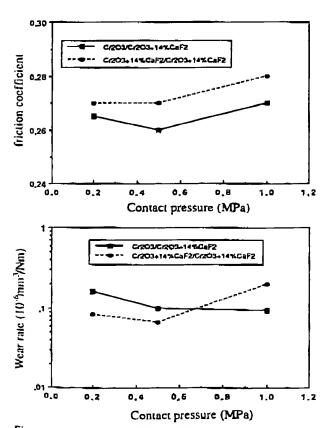


Fig. 11. Comparison of friction coefficient and wear rate of Cr₂O₃/ Cr2O3-14%CaF2 and Cr2O3-14%CaF2/Cr2O3-14%CaF2.

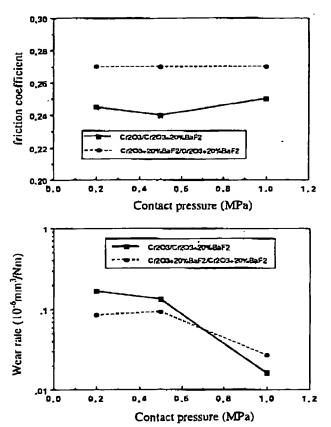
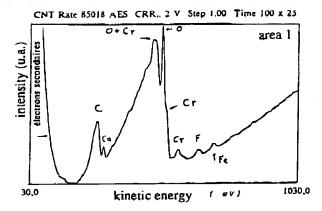


Fig. 12. Comparison of friction coefficient and wear rate of Cr₂O₃/ $Cr_2O_3-20\%BaF_2$ and $Cr_2O_3-20\%BaF_2/Cr_2O_3-20\%BaF_2$.

It is important to point out that although Cr2O3-solid lubricant coatings are less hard than pure Cr2O3 coating, the increase in critical load achieved by using a solid lubricant in the tribological case is clearly evident: for Cr₂O₃/Cr₂O₃ sliding, chevron-shaped cracks have been observed under a pressure of 14.5 MPa; however, for Cr₂O₃/Cr₂O₃-14%CaF₂ sliding, the cracking pressure increases from 14.5 (4.15) to 22.1 MPa (6.32 kN). This improvement in load capacity of the coating probably results from the reduction in friction coefficient brought about by the solid lubricant, i.e. the tangential load will decrease and consequently the critical load will obviously increase [16].

4. Characterization of the sliding surfaces and discussion

By use of Auger electron spectroscopy (AES) we have analysed the contact areas (contact plateaux) and non-contact areas of Cr2O3 and Cr2O3-14%CaF2 coating surfaces after 6 h of sliding. Figure 13 presents the results of a typical analysis of the Cr₂O₃ coating surface. We have found that the spectrum obtained in the contact area contains one calcium peak with a significant amplitude, whereas this peak does not exist in the non-



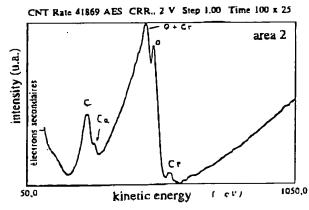


Fig. 13. Results of AES analysis of contact and non-contact areas on Cr₂O₃ surface after 6 h of sliding against Cr₂O₃-14%CaF₂ under 0.2 MPa.

contact area. These analyses indicate that sliding can enrich the solid lubricant on the surface, thus inducing an improvement in friction and wear properties.

In order to confirm this idea, a large number of analyses by energy-dispersive spectroscopy (EDS) have been carried out on different worn specimens. Figure

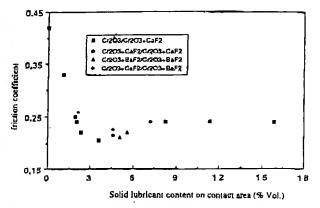


Fig. 14. Correlation between friction coefficient and solid lubricant (resulting from material transfer) content on contact area.

14 presents the relation between friction coefficient and mean solid lubricant content of three to five measurements on contact areas of various specimens. It shows that the friction coefficient first decreases with solid lubricant content if it is less than 2%-4% and then stabilizes at about 0.20-0.25 when the solid lubricant content is more than 4%. Thus the good friction and wear properties of the composite coatings probably result from the solid lubricants on contact areas producing two important effects:

- (1) a reduction in adhesion strength, which restricts the formation of adhesive junctions [11];
- (2) the presence of a soft superficial layer (CaF₂ or BaF₂) which reduces the proportion of shearing resistance at the yield point of the hard material (Cr₂O₃) [15].

5. Conclusions

- (1) The tribological performance of Cr₂O₃ coating can be improved by the incorporation of solid lubricants (CaF₂ and BaF₂). The mean friction coefficient has been reduced from about 0.4 for Cr₂O₃/Cr₂O₃ sliding to 0.2-0.25 for Cr₂O₃/Cr₂O₃-solid lubricant sliding; the friction curve of the Cr₂O₃ coatings with solid lubricant becomes much more stable than that of pure Cr₂O₃ coating.
- (2) Solid lubricant addition has also improved the wear resistance of Cr_2O_3 coating; the wear rate has been decreased from 6.5×10^{-6} mm³ N⁻¹ m⁻¹ for Cr_2O_3/Cr_2O_3 sliding to about 10^{-8} mm³ N⁻¹ m⁻¹ for Cr_2O_3/Cr_2O_3 —solid lubricant sliding.
- (3) The solid lubricant can improve the load capacity of Cr_2O_3 coating. The cracking pressure increases from 14.5 MPa (4.15 kN) for Cr_2O_3/Cr_2O_3 to 22.1 MPa (6.32 kN) for $Cr_2O_3/Cr_2O_3-14\%CaF_2$.
- (4) The optimal solid lubricant content is around 14%-21% for Cr₂O₃-CaF₂ coatings and 20%-31% for Cr₂O₃-BaF₂ coatings.

(5) Cr₂O₃-BaF₂ coatings have a lower sliding friction coefficient than Cr₂O₃-CaF₂ coatings; Cr₂O₃/Cr₂O₃-solid lubricant sliding shows a lower friction coefficient than Cr₂O₃-solid lubricant/Cr₂O₃-solid lubricant sliding. Cr₂O₃/Cr₂O₃-20%-31%BaF₂ couples display the best tribological performance under the test conditions.

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Appendix

In order to determine the wear mass precisely, it is necessary to take into account the influence of oxidation at 425 °C during the tribotest on the specimen mass. Thus three oxidation tests have been repeated under the same conditions as the tribotests, namely: environment, atmospheric air; heating rate, 200 °C h⁻¹; temperature of maintenance, 425 °C; time of maintenance, 2 h; cooling rate, in furnace.

They show that oxidation of the substrate 35CD4 (0.30%-0.37% C, 0.60%-0.90% Ni, 0.10%-0.40% Si, 0.90%-1.20% Cr, 0.15%-0.25% Mo, less than 0.035% P, less than 0.025% S) causes a mean mass gain of 1.2 mg. We have assumed that the oxidation of this steel obeys Frick's second law, i.e. $\Delta m = kt^{1/2}$.

Using a computer, we have solved the equation by a numerical method and calculated the oxidation mass after different times to heat the specimen (t_h) and to realize the tribotest at 425 °C (t_m) . Table A1 presents the results of some calculations.

TABLE A1. Oxidation mass gains of specimen substrate for different t_h and t_m

r _m (min)	Mass gain (mg)										
	th (min)										
	100	110	120	130	140	150	160	170	180		
10	0.53	0.53	0.54	0,54	0.55	0.56	0.56	0.57	0.58		
20	0.63	0.64	0.65	0.65	0.66	0.66	0.67	0.67	0.68		
30	0.73	0.73	0.74	0.74	0.75	0.75	0.76	0.76	0.77		
40	0.81	0.81	0.82	0.82	0.83	0.83	0.84	0.84	0.85		
50	0.89	0.89	0.89	0.90	0.90	0.91	0.91	0.91	0,92		
60	0.96	0.96	0.96	0.96	0.97	0.97	0.98	0.98	0.99		
70	1.02	1.02	1.03	1.03	1.03	1.04	1.04	1.04	1.05		
80	1.08	1.08	1.09	1.09	1.09	1.10	1.10	1.10	1.11		
90	1.13	1.14	1.14	1.14	1.15	1.15	1.15	1.16	1.16		
100	1.19	1.19	1.20	1.20	1.20	1.21	1.21	1.21	1.22		
110	1.24	1.24	1.25	1.25	1.26	1.26	1.26	1,26	1.28		
120	1.29	1.29	1.30	1.30	1.31	1.31	1.31	1.31	1.32		
130	1.34	1.34	1.35	1.35	1.35	1.36	1.36	1.36	1.36		
140	1.39	1.39	1.39	1.39	1.40	1.40	1.40	1.40	1.41		
150	1.43	1.43	1.44	1.44	1.44	1.45	1.45	1.45	1.45		
160	1.48	1.48	1.48	1.48	1.49	1.49	1.49	1.49	1.50		
170	1.52	1.52	1.52	1.52	1.53	1.53	1.53	1.53	1,54		
180	1.56	1.56	1.57	1.57	1.57	1.57	1.57	1.58	1.58		
190	1.60	1.60	1.61	1.61	1.61	1.61	1.61	1.61	1.62		
200	1.64	1.64	1.65	1.65	1.65	1.65	1.65	1.65	1.66		